Use of near infrared reflectance spectroscopy (NIR) to determine total carbon and total nitrogen in wetland soils

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Introduction

Near infrared spectroscopy (NIR) is a rapid, non-destructive analytical technique for quantitative analysis of organic chemicals in agricultural, food, textile, petrochemical and other industries (Malley, 1998). NIR is primarily based on absorbances by covalent bonds between H, C, O and N such as protein, starch, cellulose, carboxyl, amino acids, water and other molecules or groups. The NIR technique in actual practice combines applied spectroscopy and correlation statistics. Spectral data from the absorbance of light in the near infrared range (700-2500 nm) are correlated with concentrations or functional properties of the samples using standard reference samples. The method requires minimal sample preparation, except usually for drying. Numerous constituents can be predicted from single scans, once suitable calibration equations exist. The development of calibration equations is done separately using statistics to correlate the spectral data with the values for each constituent, parameter or function that have been obtained independently by conventional methods (reference values). Statistical methods used include multiple linear regression and partial least squares regression. Several commercial software packages are available for the recording and manipulation of spectral data, development of calibrations and prediction of constituents for unknown samples.

In the last ten years many papers have been published using the NIR technique for upland soil analysis, but very few papers exist regarding the application of NIR to wetland soil analysis (Table 1). Chemical analyses of wetland soils are often performed to investigate wetland functions here at the Olentangy River Wetland Research Park (ORWRP); however, many samples must be analyzed in order to understand temporal and spatial variations. Analyses of total carbon and total nitrogen are conducted by an external laboratory (STAR Lab in Wooster) at a price of $ 5 - 8 per sample, depending on the number of samples. Therefore, application of the NIR technique to conduct such analyses represents a great opportunity to explore, since a large number of samples might be analyzed by this technique, and only a subset of samples would need to be analyzed in an external laboratory for calibration and validation.

Research goal

The goal of this project was to find ecological applications of the NIR technique for wetland soil samples. The specific objectives were:1) to set up an NIRSystems spectrometer, model 6500, at the ORWRP analytical laboratory; 2) to determine the most suitable sampling and NIR test procedure; and 3) to apply this NIR technique for total carbon and total nitrogen analyses in wetland soil samples.

Methods

The methodology for this project included a literature review on NIR applications. After this, an NIRSystems spectrometer Model 6500 was set up in the Analytical Lab at ORWRP with the reflectance detector and Near Infrared Spectral Analysis Software (NAS) Version 3.30a for DOS. The remote reflectance module was used for scanning the samples. Air-dried soil samples taken from the experimental wetlands in spring, 2004 by C. Anderson were utilized for this study. These samples had already been analyzed for total carbon and total nitrogen by dry combustion in a C/N analyzer at the STAR Lab in Wooster, Ohio. Samples were ground and sieved (2 mm), packed into a sample cell and covered with quartz glass, then scanned by NIR. Nineteen (19) samples were utilized for calibration of the spectrometer; 22 additional samples were used for validation of total carbon, and 16 for validation of total nitrogen.

Table 1. Types of constituents and parameters that have been measured in soils by various researchers, using near infrared reflectance spectroscopy.

SOIL TYPE, LOCATION AND # OF SAMPLES	CONSTITUENT OR PARAMETER	AUTHORS
Soils from Illinois, n = 10	Organic Matter (r^2 = 0.87)	Krishnan et al., (1980)
Soils from Queensland, Australia, n = 56	Moisture (r^2 = 0.93) Organic Carbon (r^2 = 0.86) Total Nitrogen (r^2 = 0.93)	Dalal and Henry, (1986)
12 upland soils from Idaho (silt, coarse clay + silt), n = 56	Total Carbon (r^2 = 0.93) Total Nitrogen (r^2 = 0.89)	Morra et al., (1991)
Decaying litter in Wisconsin and Maine, n = 169 - 451	Total Nitrogen (r^2 = 0.94) Lignin (r^2 = 0.83) Cellulose (r^2 = 0.81)	McLellan et al., (1991)
Peat from Bog in UK, n = 36 - 65	Bulk density (r^2 = 0.97) Moisture (r^2 = 0.97) Humification (r^2 = 0.98)	McTiernan et al., (1998)
Lake sediment in Canada, n = 18	Total Carbon (r^2 = 0.93) Total Nitrogen (r^2 = 0.94) Carbonate (r^2 = 0.87)	Malley et al., (1999)

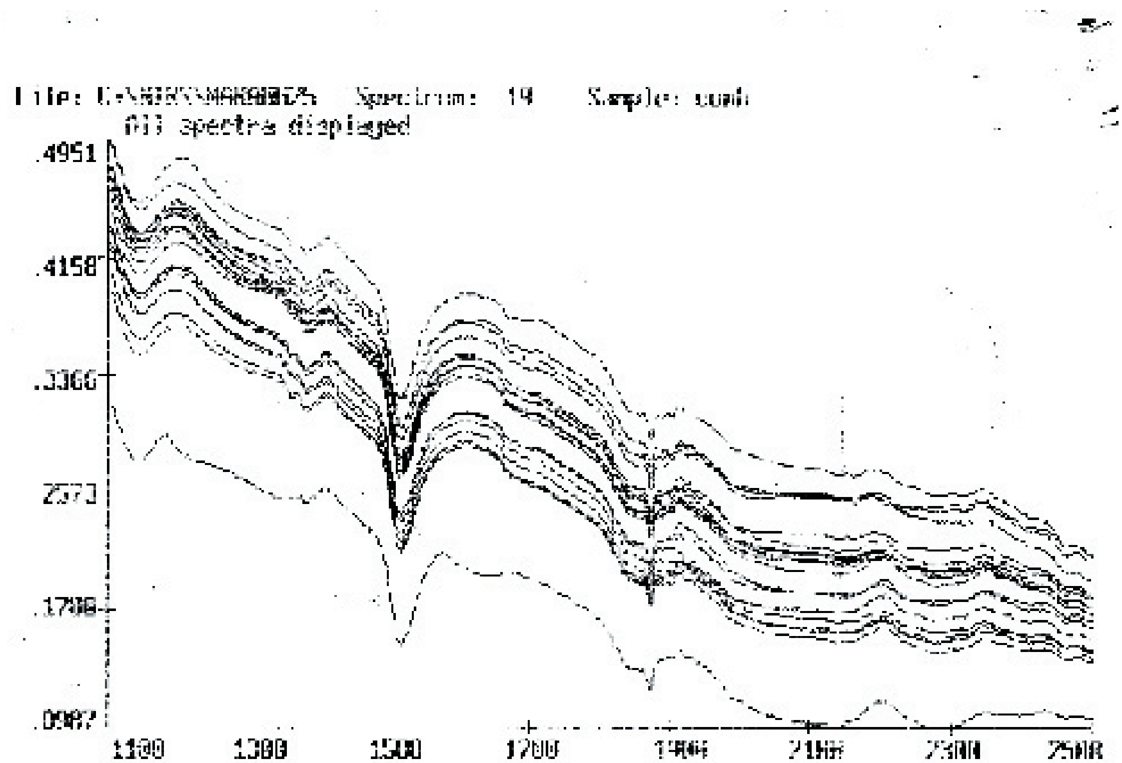

Figure 1. NIR spectra for wetland soils examined in this study.

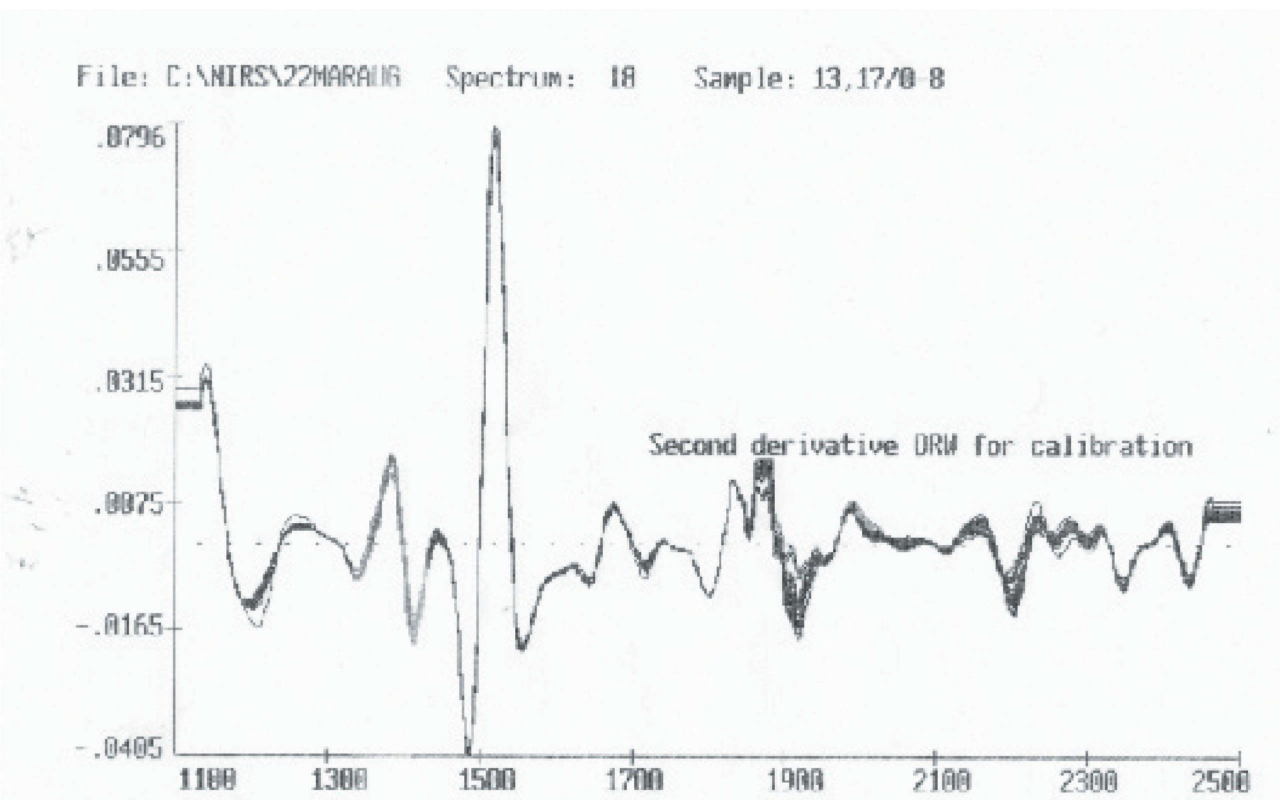

Figure 2.- Second derivative of NIR spectra for wetland soils examined in this study.

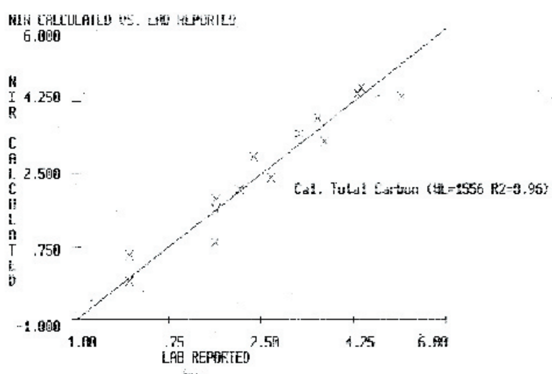

Figure 3. Calibration of spectral data (Y-axis) and laboratory analysis (X-axis) of total carbon in wetland soils. The linear relationship was calculated at 1556 nm by NAS software.

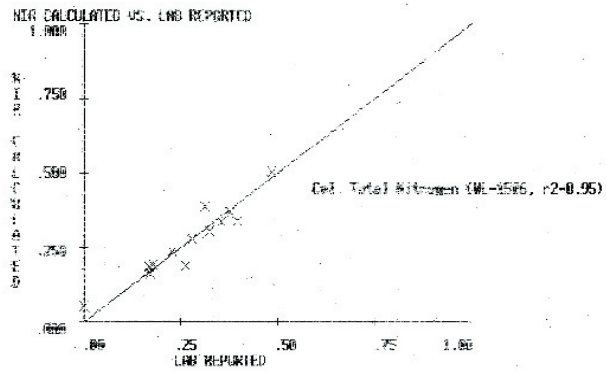

Figure 4. Calibration of spectral data (Y-axis) and laboratory analysis (X-axis) of total nitrogen in wetland soils. The linear relationship was calculated at 1506 nm by NAS software.

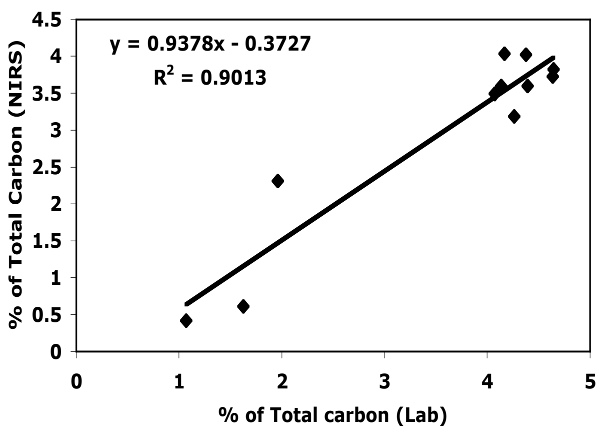

Figure 5. Validation of near infrared reflectance spectroscopy (NIRS) predicted with combustion-determined total carbon concentration in 16 wetland soil samples.

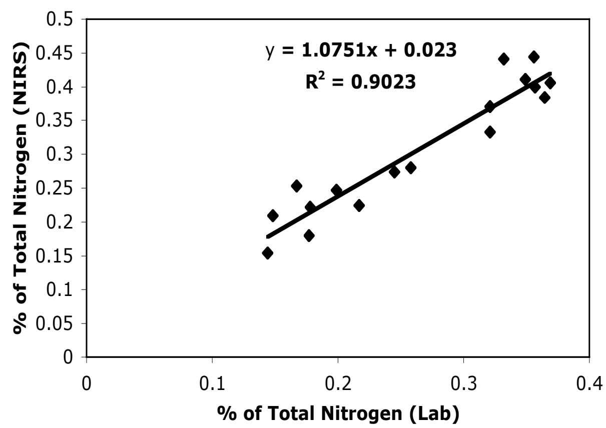

Figure 6. Validation of near infrared reflectance spectroscopy (NIRS) predicted with combustion-determined total nitrogen concentration in 22 wetland soil samples.

Results and Discussion

Quantification of Carbon and Nitrogen by NIR

The spectra of several wetland soil samples are shown in Figure 1. All samples showed absorbance peaks in the 1500 nm, 1900 nm and 2200 nm regions. The peak in the region of 1500 nm is the result of near infrared absorption by N-H bonds such as amine (RNH_3) groups. Between 1900 nm and 2000 nm, H_2O and C=O bonds are responsible for absorption peaks. In the region of 2100 and 2200 nm, N-H and O-H combinations show absorption peaks. The peak in the region of 1500 nm is the result of near infrared absorption by N-H bonds such as amine (RNH_3) groups. Between 1900 nm and 2000 nm, H_2O and C=O bonds are responsible for absorption peaks. In the region of 2100 - 2200 nm, N-H and O-H combinations show absorption peaks. Soil organic matter in wetlands is composed of several complex organic molecules with various functional groups that caused the absorption peaks previously described. The spectra were transformed to the second derivative (Figure 2) using NAS software. From these spectral data and concentrations of total carbon (19 samples), a calibration curve was created using standard regression.

Calibration

The software created four calibration curves derived from the functionality of four wavelengths shown in Table 2. According to r^2 correlation coefficients, the optimal linear relationship based on a single wavelength for total carbon content in wetland soil was observed at 1556 nm (Figure 3). The same procedure was carried out for total nitrogen

Table 2. Linear relationships between spectral data and laboratory analysis of wetland soils. The relationships were calculated at different wavelengths by NIRS model 6500 using the NAS software.

Wavelength (nm)	Near Infrared Absorptions	r^2
Total Carbon:		
2332	C-H + C-H combinations	0.8019
2170	N-H combinations	0.8721
2042	C=O, O-H combinations	0.9155
1556	N-H	0.9614
Total Nitrogen:		
2332	C-H + C-H combinations	0.748
1598	Ar-CH, C-H	0.8731
2322	C-H + C-H combinations	0.9142
1506	N-H	0.9422

concentration (Table 2); for this element the optimal linear relationship was obtained at 1506 nm (Figure 4).

Validation

The calibration curves with highest r^2 were chosen to create a routine analysis file on NAS software. Using the routine analysis software mode for total carbon and total nitrogen, 20 samples were scanned and the concentrations of total C and N were calculated. The concentrations of total carbon and nitrogen were determined previously in a C/N carbon analyzer; thus, these samples were utilized for validation of the NIR technique. Figures 5 and 6 illustrate the comparisons of total carbon and total nitrogen obtained by conventional laboratory methods, vs. total C and N obtained by NIR. Despite the small number of samples utilized for calibration and validation, a good linear correlation was found between the results obtained with the C/N analyzer and the concentrations obtained by NIR. For total carbon, r^2 values between 0.90-0.93 have been reported for upland soils, and for total nitrogen, coefficients of 0.89-0.94 have been described for upland soils and lake sediments (Dalal and Henry, 1986; Malley et al.,1999; McLellan et al., 1991; Morra et al., 1991). The linear correlations found in this study are within the range reported in the literature for other types of soil.

Conclusions

The remote reflectance module was found to be the most adequate sample module for scanning wetland soils in the NIRSystems instrument model 6500. A small sample size proved adequate for calibrating and validating NIR spectral data on total carbon and nitrogen contents of ORWRP wetland soils with laboratory-determined values for these parameters. For total carbon content the optimal wavelength was observed at 1556 nm, and for total nitrogen content it was observed at 1506 nm.

A calibration using two wavelengths should improve the linear relationship even further. NIR has great potential for application in routine carbon and nitrogen analyses of wetland soils and plant material. A big advantage is that both carbon and nitrogen values can be determined from the same NIR spectra.

Acknowledgments

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